

Automatic Analysis of Dissolved Metal
Pollutants in Water by Energy Dispersive
X-Ray Spectroscopy

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16. ABSTRACT An automated system for the quantitative determination of dissolved metals such as Fe, Cu, Zn, Ca, Co, Ni, Cr, Hg, Se, and Pb in water is described. The system collects a water sample, preconcentrates the dissolved metals with ion-exchange paper automatically in a sample collection and preparation module (SCPM) controlled by a microprocessor computer, and then quantitates the metals with an energy-dispersive x-ray spectrophotometer. It has been demonstrated in the laboratory that the system can automatically and simultaneously quantitate dissolved multi-element metal ions in water in the concentration range of parts per million to parts per billion.		
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Automatic analysis of dissolved metal pollutants in water

BY ENERGY-DISPERSIVE X-RAY SPECTROMETRY

RECENT CONCERN about the effect of trace amounts of heavy metals in water has led to an increasing need to monitor the quality of surface water and groundwater as well as water supplies and effluents for heavy metals.

The status of analytical methodology for trace metals, reviewed and discussed by Kopp,¹ shows that atomic absorption (AA) is the most widely used technique. Although AA is a precise, easily used technique, it suffers from the disadvantage of being essentially a single-element determination, as well as sometimes requiring complicated sample preparation. Flame emission spectroscopy is used for elements such as the alkali metals and alkaline earths, but is not sufficiently sensitive for other elements. Plasma emission, particularly the inductively coupled argon plasma, looks most promising in the area of simultaneous multielement capability, but requires quite expensive instrumentation. All these methods require that the water sample be transported to the laboratory for analysis. For large numbers of samples, this can entail considerable expense; however, of more concern is the possible loss of trace elements by improper preservation.

The recent development of both semiconductor detectors, which have excellent energy resolution, and advanced microcomputers, used in data acquisition and reduction, has made energy-dispersive x-ray fluorescence (XRF) a simple, rapid, and versatile analytical tool for determination of dissolved metal ions in water.

For this reason, XRF appears to be of value as a

rapid field monitoring technique for metals in water. It is nondestructive, and requires little or no sample preparation or sample transport. The dissolved metals in the wastewater sample either can be measured directly as a liquid sample² or can be measured after the sample has been collected on ion-exchange resin-loaded filter paper.³⁻⁶ XRF has an additional advantage, namely an inherent capability of simultaneous multielement analysis.

In order to use the XRF technique successfully as a field instrument in conjunction with the use of ion-exchange resin-loaded filter paper for collecting dissolved metals, it is critical to have a system that can automatically sample and preconcentrate the water sample. Under an EPA contract, Magnavox has developed a system that automatically and continuously measures the dissolved metals in aqueous samples.⁷ The system and its applications are described in this paper.

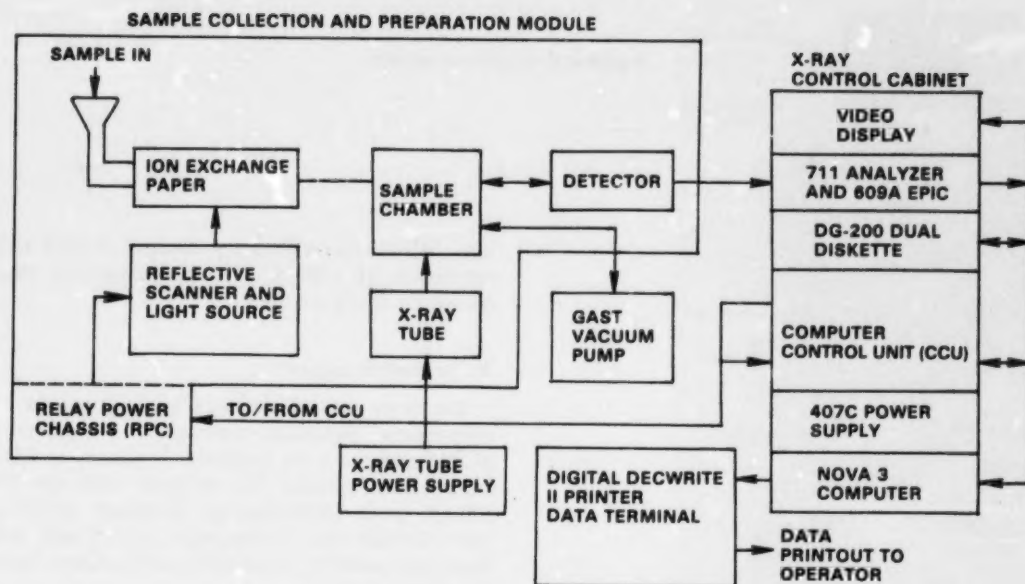
X-ray spectroscopy system

A block diagram of the system (*Figure 1*) shows its various components. It has two main components, the sample collection and preparation module (SCPM) with relay power chassis and x-ray unit attached to it, and the x-ray control cabinet. A detailed description of the system follows.

Sample collection and preparation module

The SCPM (*Figures 2 and 3*) consists of a sample tank, a roll of 1½-in.-wide ion-exchange resin-loaded filter paper on a supply reel, a filter-paper transport mechanism, a collection tank, and a spent-water tank. A water sample as large as 500 mL can be processed from the sample tank through the ion-exchange filter paper and into the collection tank. The water in the collection tank will either recycle back to the sample tank or go to the spent-water tank. The water transport lines and tanks of

Dr. Ho is Chemical Engineer, and Dr. Lin is Mechanical Engineer, Environmental Monitoring and Support Laboratory—Cincinnati, U.S. Environmental Protection Agency. Any mention of product names in this article is not intended to imply an endorsement by the U.S. Environmental Protection Agency. The authors wish to acknowledge Mr. John P. Donnelly for assisting in modifying and troubleshooting the system during the course of this study.



SCPM are made of plexiglass and Teflon in order to reduce the possibility of sample contamination. The filter-paper transport mechanism includes a precision motor that moves the filter paper forward and backward in precise increments, a photoelectric sensor that detects seams in the paper, a cutter, and a transporter that moves the cut filter paper to the x-ray chamber for analysis.

Relay power chassis

The relay power chassis contains the relays that control the SCPM and its relay drivers, electronics for the water-presence sensor, and photoelectric control. The water-presence sensors, the photoelectric control associated with the tape sensor optics,

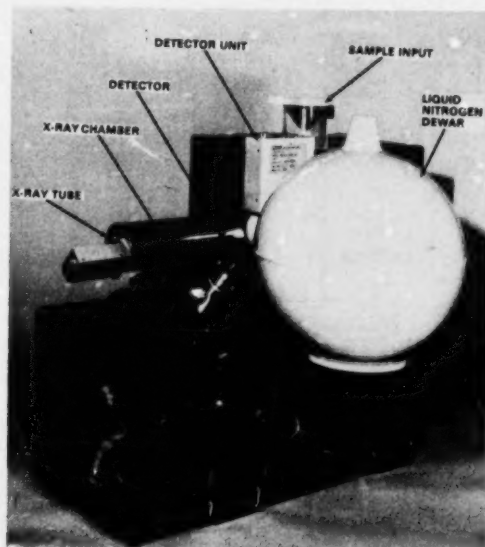


Figure 2 Sample collection and preparation module.

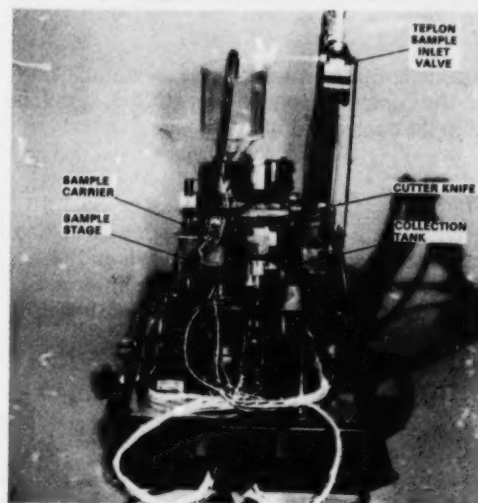


Figure 3a View of internal components of SCPM.

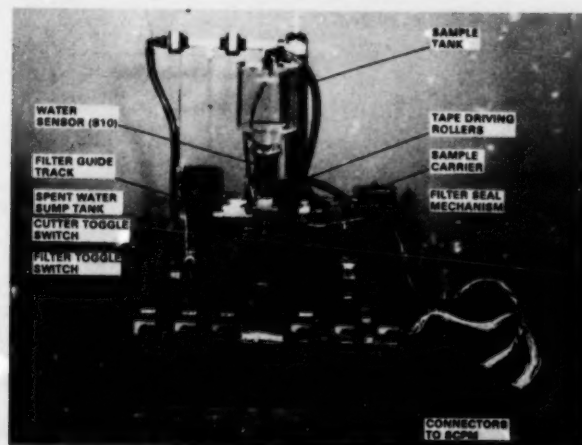


Figure 3b View of internal components of SCPM.

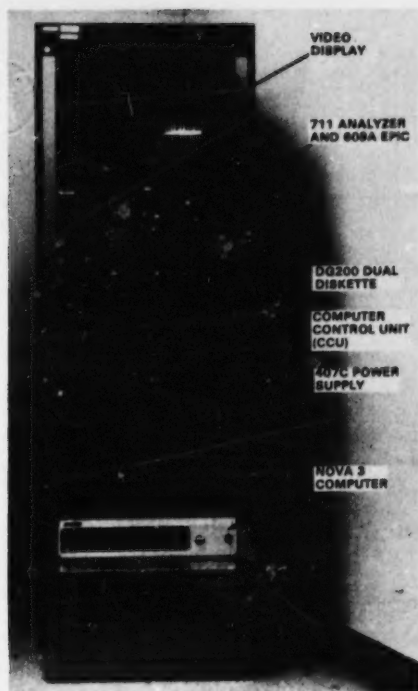


Figure 4 X-ray control cabinet.

ium-drifted silicon detector 30 mm² in area with a resolution of 180–190 ev. The detection unit is cooled by liquid nitrogen.

X-ray control cabinet

The x-ray control cabinet (Figure 4) provides the operational functions necessary to operate the SCPM and the x-ray analyzer. It houses an EDAX International model 711 analyzer and the 609A EDAX peak identification computer (EPIC), a video display unit, a computer control unit, and a Nova computer in conjunction with a Data General dual floppy diskette.

Analyzer 711 and EPIC 609A and video display

The 711 analyzer controls the energy range, the time of analysis, window selection, video display mode, and other operations of the x-ray equipment. It also contains the multichannel analyzer that stores the spectra generated by a detector. The 609A EPIC is the EDAX peak identification computer, and is used to identify the peaks in the spectra by generating K, L, and M markers. It has the added capability of generating sample identification information on the video display. This provides for visual observation of the spectra both during and after analysis.

and various limiting switches serve as status detectors for the computer control unit (CCU), which is located in the control cabinet.

X-ray unit

The x-ray unit consists of the x-ray tube and chamber, the detector unit, and a 10-L liquid nitrogen Dewar. The x-ray tube is a rhodium-targeted, air-cooled, pulsed unit. The detection unit is a lith-

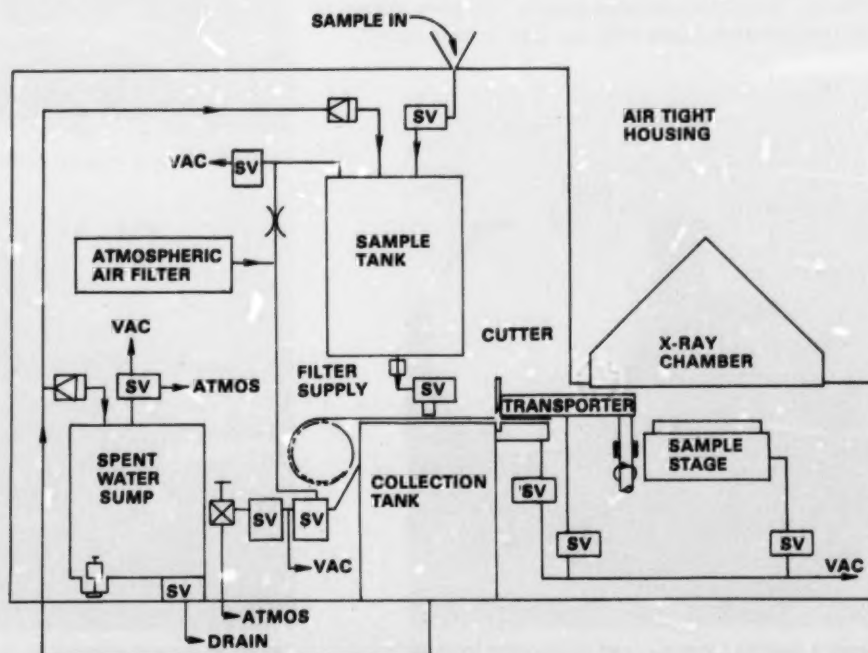


Figure 5 SCPM system flow diagram.

Computer control unit

The computer control unit interfaces with the relay power chassis to control the operation of the SCPM. It also interfaces with the Nova 3 computer and the 711 EDAX analyzer for analyzing the sample automatically.

Nova computer and Data General floppy diskette

In conjunction with the Data General dual floppy diskette, the Nova 3 computer provides the computational capabilities of the x-ray system. It has a 32-K memory and can be programmed in BASIC and extended BASIC languages. The dual floppy diskette provides the storage of the spectra and different mathematical and statistical computer programs.

Operational procedures

Sample handling

The SCPM (*Figure 5*) processes the water samples through resin-loaded filter paper in which the metal ions contained in the samples are concentrated by the ion-exchange resins. Once this is completed, the filter paper is then ready for x-ray analysis.

The water first enters the sample tank, where its presence is detected by a water sensor located between the sample tank and the collection tank and above the filter-paper tape. The sensor consists of two ceramic transducers which are mounted facing each other across the neck of the sample tank, one transducer acting as a transmitter and the other as a receiver. When water is present, it acts as a medium for the signal. When no water is in the tank, the air gap prevents the receiver from receiving the signal from the transmitter. This signal is rectified and filtered to operate the logic in the microprocessor controller.

When water is present in the sample tank, a vacuum is applied to the collection tank and a solenoid valve is opened in the neck of the sample tank, allowing water to pass to the collection tank through the filter-paper tape positioned between the tanks. The number of times that the water is recycled through the filter paper is controlled by the setting on the control panel of the microprocessor. All the water movement in the SCPM is handled by a Gast vacuum pump. The housing for the SCPM is airtight, and all the air entering the SCPM is filtered to prevent contamination of the sample.

After the water sample has been filtered and the metal ions have been collected on the ion-exchange

filter paper, the filter tape is air-dried and moved to the cutter stage in precise increments by a motor-driven mechanism. The filter tape is cut on the cutter stage while being held in place by vacuum, and is then transported to the sample stage where it is inserted into the x-ray chamber by raising the sample stage against the bottom of the chamber. The sample stage seals the chamber and prevents the escape of x-rays.

While the sample is being irradiated, the filter tape is retracted behind the sample collection orifice and the spent water is driven by vacuum from the collection tank into the spent-water sump tank and subsequently to the waste collection tank. The sump float magnetic switch then signals that the system is empty and ready for flushing.

Flushing is critical in the prevention of cross contamination of the water samples, and as a result, it is necessary to flush the sampling system after each sample acquisition. This is accomplished by passing two 500-mL volumes of flush water through the sampling system. The flushings are subsequently discharged.

After the analysis and flushing have been completed, the sample stage returns to the transporter level where the transporter retrieves the sample from the sample stage, deposits it in the sample retrieval chute, and then returns to the cutter stage position. The retrieved sample may be removed from the retrieval chute through the sample retrieval door.

X-ray analysis

Energy-dispersive x-ray analysis is a multielement technique inasmuch as all the elements present on the filter paper are measured simultaneously. The sample is excited by an x-ray tube, and the secondary x-rays subsequently generated are detected. The pulse x-ray tube, which is coupled to the x-ray detector, is turned off when the detector processes the incoming x-rays from the sample, permitting a more efficient collection of the incoming x-rays. The net effect of using a pulse x-ray tube is the storage of more counts, or incoming x-rays, per unit of time, which therefore shortens analysis time. A preamplifier takes the charge, or pulse, presented by the detector and converts it to a voltage signal proportional to the energy deposited on the detector. A main amplifier then takes the preamplifier signals and amplifies them for presentation to the multichannel analyzer (MCA).

The multichannel analyzer qualitatively and quantitatively extracts information from the input signal and generates the spectra which are stored in

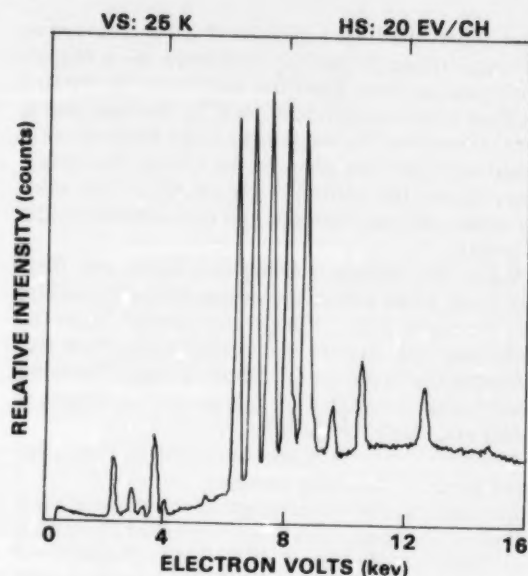


Figure 6 Energy-dispersive x-ray spectra.

either a 400- or an 800-channel memory of MCA and also are presented on video display. The spectra in the analyzer are then transferred to the computer memory by the user with the aid of the Digital Decwrite II terminal. The spectra in the computer memory are recorded onto a diskette file for later processing. When needed, the spectra stored in the floppy diskette can be transferred back to the computer memory and video-displayed. The spectra can also be plotted as shown in Figure 6 by a Tektronix 4662 interactive digital plotter.

To unfold individual peaks for each element in the spectra, the user enters the centroid energy of the peak to be stripped. A computer program that considers the energy distribution at this peak to be a Gaussian function will calculate the maximum height of the peak based on its shape. The standard deviation σ of this Gaussian distribution at this peak is determined by the following equation:

$$\sigma = \frac{0.6}{\sqrt{2}} \text{ FWHM}$$

where

$$\begin{aligned} \text{FWHM} &= \text{the full width of half maximum} \\ &= \frac{\sqrt{R^2 + 2550(E - 5.894)}}{1000} \end{aligned}$$

and where R = the spectrometer resolution in ev and E = the desired centroid energy in kev.

Once the energy distribution at this peak is established (background at this peak is automatically eliminated), the net intensity is counted within a window of 1.2 FWHM in the spectrum. A plot of such stripped spectra, as shown in Figure 7, is typical for a sample containing several elements.

The net intensities of individual peaks are stored in the diskette for further analysis. With the known concentrations C_i and calculated net intensities I_i , the following equation is used to generate a calibration curve:

$$C_i = S_i I_i + B_i$$

where S_i and B_i are the slope of the calibration curve and the intercept, respectively, for element i . The coefficients S_i and B_i are then calculated by a least squares fit. An example of the calibration curve for several elements is shown in Figure 8.

Examples of applications

A laboratory investigation of the Magnavox system was conducted by analyzing aqueous solutions of 10 metal ions. They included Ca, Fe, Co, Ni, Cu, Zn, Pb, Hg, Cr, and Se. The first seven metals were easily exchanged on a strong acid resin-loaded SA-2 filter paper. Hg, Se, and Cr, which could not be retained by SA-2 filter paper, were collected on a strong base resin-loaded SB-2 filter paper.

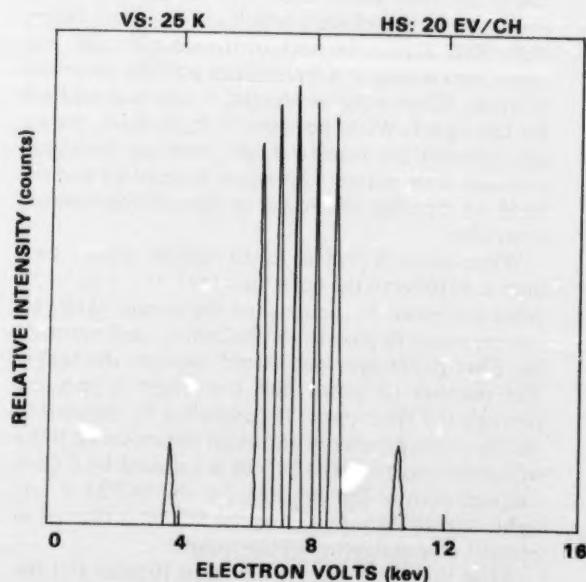


Figure 7 Stripped energy-dispersive x-ray spectra.

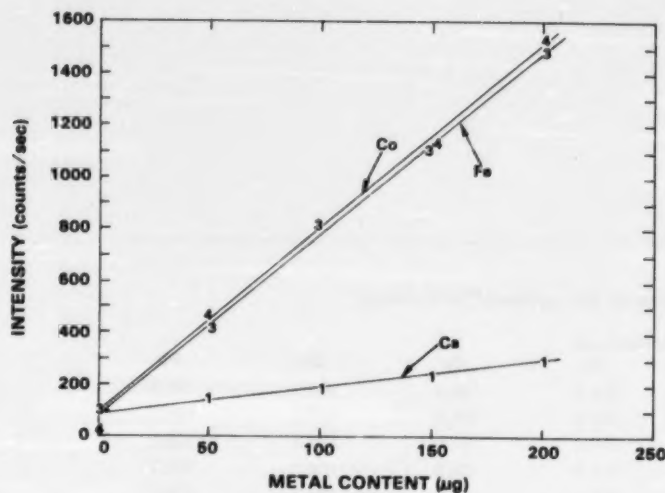


Figure 8 Calibration curves for Co, Fe, and Ca analysis on SA-2 filter paper.

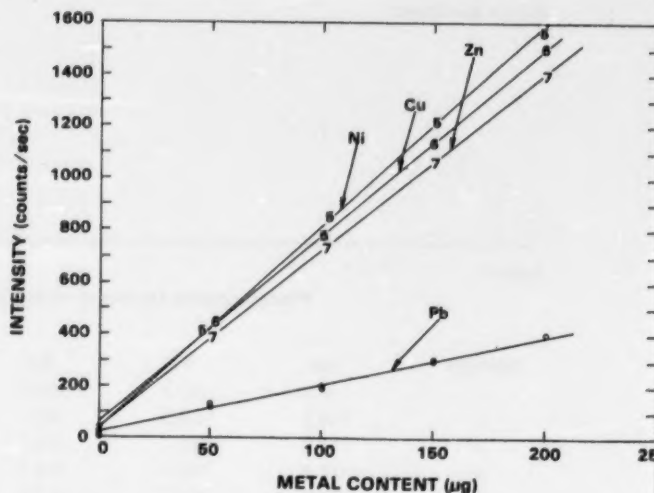


Figure 9 Calibration curves for Ni, Cu, Zn, and Pb analysis on SA-2 filter paper.

Reagents and materials

Atomic absorption standard solutions of 10 metals at a concentration of 1000 mg/L traceable to National Bureau Standards from MCB Manufacturing Chemists, Inc., were used as stock solutions. Rolls of SA-2 and SB-2 resin-loaded filter-paper tape were custom-manufactured by Whatman, Inc. The SA-2 paper contained Amberlite IR-120 ion-exchange resin, a high molecular weight copolymer of polystyrene sulfonic acid cross-linked with divinyl benzene, supplied in the sodium form. The SB-2 paper contained Amberlite IRS-400 ion-exchange resin, a high molecular weight copolymer of polyvinyl benzyl trimethylammonium hydroxide cross-linked with divinyl benzene, supplied in the chloride form.

Method of analysis

A working standard solution containing 10 mg/L each of Ca, Fe, Co, Ni, Cu, Zn, Pb, Hg, Cr, and Se was prepared by adding aliquots of the individual stock metal solutions to a volume of Millipore Super Q deionized water. Test solutions were prepared by diluting aliquots of the 10-mg/L working standard solution to 1-L volumes and adjusting to the desired pH by adding nitric acid. The optimum pH was between 2 and 4 (Ref. 8), and a pH of 3 was selected for this study. After adjusting the pH to 3, one 500-mL aliquot was passed through SA-2 filter paper in the SCPM, and the other 500-mL aliquot was passed through SB-2 paper. Ca, Fe, Co, Ni, Cu, Zn, and Pb were subsequently determined in the SA-2 paper, and Hg, Cr, and Se were measured in the SB-2 paper. In order to achieve maximum ion exchange, it was necessary to repeat the filtration process until equilibrium was achieved between the filter and the solution. For 200 μg of each of the 10 metals in the 500-mL aliquot, equilibrium was reached after three or four filtrations. Four filtra-

tions were used in all subsequent tests. The quantitative analysis began by preparing standard solution samples and obtaining calibration curves. The quantity of metal ion in an unknown sample could then be calculated from the calibration curve. Recovery rates were measured on several samples of the same concentration and expressed as the ratio of the detected amount and the added known amount.

Results and discussion

Calibration plots for the 10 metals are shown in Figures 8, 9, and 10. The net x-ray intensities were expressed in counts per second and the concentrations were expressed in micrograms (μg). For each metal ion, a straight line was obtained for samples in the metal ion contents ranging from 50 to 200 μg in a 500-mL solution.

The precision and recovery rates of analysis were measured on seven individual samples containing 100 μg each of 10 metal ions which were filtered

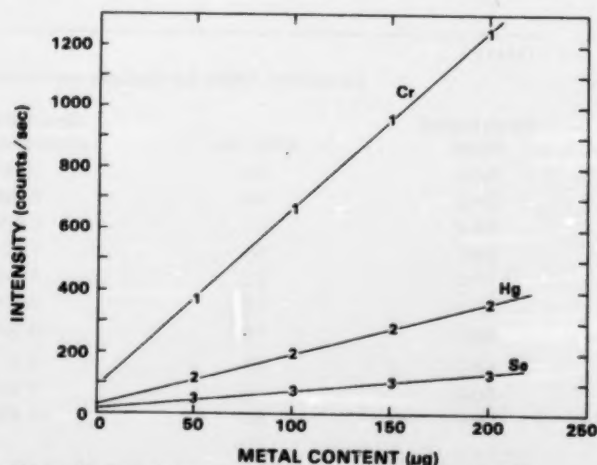


Figure 10 Calibration curves for Cr, Hg, and Se analysis on SB-2 filter paper.

Table 1

Precision and recovery of metal ions at 100- μ g level (SA-2 paper)

Sample	Ca	Fe	Co	Element, μ g Ni	Cu	Zn	Pb
1	116.8	103.4	105.4	104.6	104.1	104.6	107.5
2	116.7	105.3	107.7	107.8	105.5	107.3	105.1
3	117.5	105.4	108.7	107.6	107.0	107.1	106.3
4	113.2	103.0	106.3	104.9	104.5	104.3	105.7
5	114.9	106.3	107.6	107.1	106.8	107.7	108.0
6	110.3	102.2	105.5	104.9	104.1	104.1	107.7
7	111.2	102.9	105.5	104.9	103.3	104.8	106.2
$\bar{X}$	114.4	104.1	106.7	106.0	105.0	105.7	106.6
Std. dev.	2.87	1.57	1.33	1.45	1.43	1.58	1.1
Rel. std. dev.	2.51%	1.50%	1.24%	1.37%	1.36%	1.50%	1.03%
% recovery	114.4	104.1	106.7	106.0	105.0	105.7	106.2

through SA-2 filter paper. The results are given in Table 1. The precision was between 1% to 2% relative standard deviation for the seven metals recovered on SA-2 filter paper. The recovery was slightly greater than 100%, probably because of some systematic bias in the calibration curves.

The sensitivity of this preconcentration technique can be represented by detection limits C_{DL} . The detection limit C_{DL} is defined as the peak count corresponding to the element that must rise above the background count by at least twice the standard deviation of the background, which gives a 95% confidence limit.⁹ By using that definition, it is possible to express the detection limit as $C_{DL} = 2\sqrt{B}/I$, where C_{DL} is the concentration, B is the background

count, and I is the peak count per unit of concentration, for example, counts/ μ g. Table 2 shows the detection limit for the 10 metal ions based on a 100-sec analysis time. The detection limit for these 10 metal ions varies from 0.54 μ g/L for Fe to 9.14 μ g/L for Se. It is important to recognize that the detection limit that can be achieved using this concentration technique is a function of the volume of liquid sample that can be handled. If the system can process more than 500 mL of sample, a lower detection limit can be achieved.

Conclusion

This automated XRF system has demonstrated

Table 2

Detection limits for various metal ions in SA-2 and SB-2 resin-loaded papers

Resin-loaded paper	Metal ion	Spectral line measured, kev	Detection limit, ^a μ g/cm ²	Detection limit, ^b μ g/L
SA-2	Ca	3.690	0.21	1.00
SA-2	Fe	6.398	0.11	0.54
SA-2	Co	6.924	0.15	0.70
SA-2	Ni	7.471	0.15	0.74
SA-2	Cu	8.040	0.19	0.90
SA-2	Zn	8.630	0.21	1.00
SA-2	Pb	10.550	0.79	3.80
SB-2	Cr	5.411	0.24	1.04
SB-2	Hg	9.987	0.91	4.36
SB-2	Se	11.207	1.90	9.14

^aBased on 2.4-cm² area.

^bBased on 500-mL sample.

the potential capability to measure multielement metal ions in water automatically and simultaneously. Good precision and accuracy were obtained in the parts per million to parts per billion levels under laboratory tests.

Further research is needed to study the effect of suspended solids in the water sample and also to develop a more universal resin-loaded filter paper capable of ion exchange over a wide range of metal ions. After this has been accomplished, this system could become an effective monitor for field installation. Samples filtered and analyzed at the sampling site could greatly reduce the possible loss of trace metals during transport and storage.

The system is easy to operate, and it does not require a skilled operator to perform accurate and precise analyses. It quantitatively determines known metal pollutants or those suspected to be present. In addition, it also qualitatively determines unsuspected metal pollutants from the multielement spectra it produces. This greatly increases the significant information useful in the area of water management.

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